

Two-dimensional magnetism in κ -(BEDT-TTF)₂Cu[N(CN)₂]Cl, a spin-1/2 Heisenberg antiferromagnet with Dzyaloshinskii-Moriya interaction

Ágnes Antal,¹ Titusz Fehér,¹ Bálint Náfrádi,^{1,2} László Forró,² and András Jánossy^{1,*}

¹*Budapest University of Technology and Economics,
Department of Physics and Condensed Matter Research Group of the
Hungarian Academy of Sciences, P.O. Box 91, H-1521 Budapest, Hungary*

²*Institute of Physics of Complex Matter, FBS, Swiss Federal Institute of Technology (EPFL), CH-1015 Lausanne, Switzerland
(ΩDated: October 22, 2012)*

Field-induced antiferromagnetic (AF) fluctuations and magnetization are observed above the (zero-field) ordering temperature, $T_N = 23$ K by electron spin resonance in κ -(BEDT-TTF)₂Cu[N(CN)₂]Cl, a quasi two-dimensional antiferromagnet with a large isotropic Heisenberg exchange interaction. The Dzyaloshinskii-Moriya (DM) interaction is the main source of anisotropy, the exchange anisotropy and the interlayer coupling are very weak. The AF magnetization is induced by magnetic fields perpendicular to the DM vector; parallel fields have no effect. The different orientation of the DM vectors and the g factor tensors in adjacent layers allows the distinction between interlayer and intralayer correlations. Magnetic fields induce the AF magnetization independently in adjacent layers. We suggest that the phase transition temperature, T_N is determined by intralayer interactions alone.

PACS numbers: 76.30.-v, 76.50+g, 75.30-m

One-dimensional (1D) magnets, i.e., isolated chains of magnetic atoms or molecules have no ordering phase transitions while 3D magnets order at finite temperatures, T_N . Magnetic ordering in two dimensions, i.e., in isolated planes, is a delicate question [1]. Theory predicts for most anisotropic two-dimensional (2D) magnets a phase transition at finite T_N except if ordering breaks a continuous symmetry. The case of $S = 1/2$ anisotropic Heisenberg antiferromagnets is complicated [2]. Experiments on low dimensional magnets with negligible interactions between the magnetic chains or planes are rare. The magnetic-field-induced change in the excitation spectrum of 1D Heisenberg chains [3, 4] agrees with theory [5, 6]. Field-induced magnetism has also been studied in a quasi 2D $S = 1$ dimer system [7]. The present experiments are on a quasi 2D, $S = 1/2$ magnet where the continuous symmetry is broken by a very small anisotropy and the applied magnetic field, H .

κ -(BEDT-TTF)₂Cu[N(CN)₂]Cl (κ -ET₂-Cl) is a layered spin 1/2 Heisenberg antiferromagnet with a magnetic ordering transition [8] at $T_N = 23$ K measured [9] in $H = 0$. The ET molecules are arranged in a 2D lattice of singly charged dimers. The electronic band is effectively half filled and the system is on the insulating side of a nearby metal-insulator Mott transition. The two chemically equivalent organic ET layers [10, 11], A and B (Fig. 1) are separated by Cu[N(CN)₂]Cl polymer sheets.

The ordered state is well described by two-sublattice antiferromagnetic layers weakly coupled through the polymeric sheets [12]. The measured macroscopic parameter of the in-plane isotropic exchange, $(J/2) \sum_{i,j} \mathbf{S}_i \cdot \mathbf{S}_j$ is $\lambda M_0 = 2J/(g\mu_B) = 450$ T [8, 13]. The magnitude of the antisymmetric Dzyaloshinskii-Moriya (DM) ex-

change interaction, $(1/2) \sum_{i,j} \mathbf{D}_{ijl} \cdot (\mathbf{S}_i \times \mathbf{S}_j)$ is $DM_0 = 2D_{12}/(g\mu_B) = 3.7$ T [12, 14]. \mathbf{D}_A (\mathbf{D}_B) is aligned $\varphi_0 = 134^\circ$ (46°) from \mathbf{a} in the (\mathbf{a}, \mathbf{b}) plane [14]. [The summation is over the four first-neighbor dimers i and j [Fig. 1(b)], $l = A, B$. M_0 is the $T = 0$ sublattice magnetization. The length of the (\mathbf{a}, \mathbf{b}) plane component of the DM interaction, $D_{12} = |D_{ijl}^{ab}|$ is the same for all pairs]. The continuous rotational symmetry around the DM vector is nearly perfect in the absence of H ; the coupling between planes and the in-plane anisotropy of the exchange are all of the order of 1 mT [12].

The peak temperature T^* in the nuclear spin relaxation rate, $1/T_1$, often identified with the onset of the magnetic order [15], increases significantly with H [16]. This is surprising since in usual antiferromagnets with no anisotropic interactions the order is little affected by H . Hamad *et al.* [16] explained changes in $1/T_1$ under pressure near T_N by the frequency dependence of the spin fluctuation spectrum. In their theory, spin fluctuations depend on the frustration of the exchange interactions in the triangular lattice of the ET dimers. The theory fails, however, to account for the increase in T^* with increasing NMR frequency.

Kagawa *et al.* [9] pointed out that in κ -ET₂-Cl the DM interaction plays an important role above T_N . In magnetic fields (unless parallel to the DM vector) the phase transition is replaced by a crossover. In this case the AF magnetization remains finite above T_N and there is a weak ferromagnetic moment along \mathbf{H} at all temperatures. They measured μ_s , the field-induced staggered static magnetic moment per sublattice site, to temperatures well above T_N by NMR. They explain the increase of T^* , with H by a shift to higher temperatures of the finite peak in the temperature dependence of $\chi(Q_{AF}, \omega = 0)$

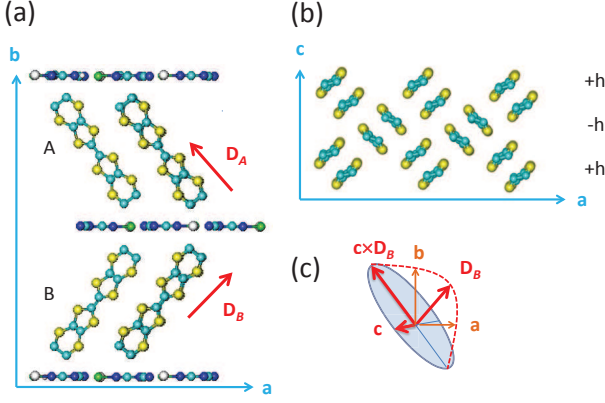


FIG. 1. (Color online) Structure of κ -ET₂-Cl. (a) Projection along \mathbf{c} onto the (\mathbf{a}, \mathbf{b}) plane. Only two ET molecules per plane are shown for clarity. The Dzyaloshinskii-Moriya vectors of the A and B layers, \mathbf{D}_A and \mathbf{D}_B are oriented differently in the (\mathbf{a}, \mathbf{b}) plane. (b) The 2D magnetic ET layer projected along the long ET molecular axis onto the (\mathbf{a}, \mathbf{c}) plane. The effective field, \mathbf{h} , due to the DM interaction alternates along \mathbf{c} . (c) Magnetic field orientations of ESR measurements in layer B . The field-induced magnetization in the plane perpendicular to the DM vector (blue ellipse) shifts and broadens the ESR.

replacing the divergence in $H = 0$ at T_N . Their mean field model describes qualitatively the H dependence of the static staggered susceptibility, $\chi(Q_{AF}, \omega = 0)$ but unrealistic exchange interaction parameters are required for a quantitative agreement.

In this paper we study the electron spin resonance (ESR) in κ -ET₂-Cl above T_N in fields up to 15 T. The field-induced staggered magnetization, \mathbf{M}_s shifts the resonance field. Fluctuations of \mathbf{M}_s enhance the transverse spin relaxation rate, $1/T_2$ and increase the ESR linewidth, $\Delta H = (\gamma T_2)^{-1}$. The fluctuations increase rapidly with increasing \mathbf{H} in the plane perpendicular to \mathbf{D} , while fields parallel to \mathbf{D} have no effect. The difference in the orientation of the DM vectors and the g factor tensors in adjacent weakly coupled A and B layers [Fig. 1(a)] allow the distinction between interlayer and intralayer correlations. Above T_N , \mathbf{H} affects the magnetic order in adjacent layers independently. We suggest that in zero external field T_N depends on intralayer interactions alone, i.e., it is the magnetic ordering temperature of the isolated 2D molecular plane. The nature of the order in the third dimension (i.e., from plane to plane) is uncertain. Furthermore, we propose that the increase in T^* with field in κ -ET₂-Cl arises from a low frequency field-induced gap.

Single crystals of κ -ET₂-Cl were grown by the standard electrochemical method. Crystal quality was verified by X-ray diffraction. The ESR spectrometers [17, 18] operate at 111.2 and 222.4 GHz at BME [17] and at 9, 210 and 420 GHz at EPFL [18]. The fluctuation spectrum is field

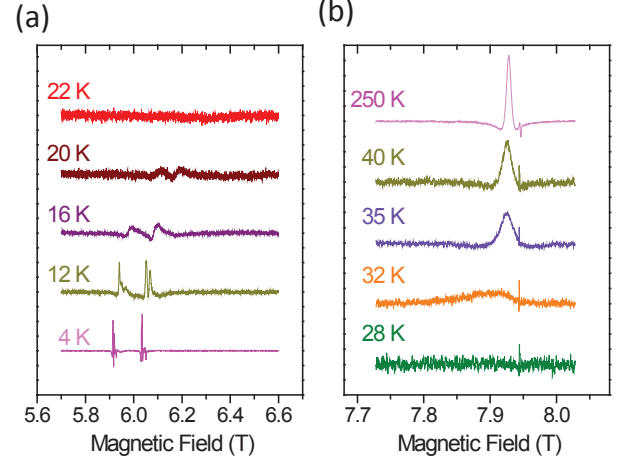


FIG. 2. (Color online) Temperature dependence of κ -ET₂-Cl ESR dispersion derivative spectra at 222.4 GHz frequency and $\mathbf{H} \parallel \mathbf{c}$ magnetic field. The relative amplitudes at different temperatures are arbitrary. (a) Two antiferromagnetic resonance modes below $T_N = 23$ K. (b) ESR in the paramagnetic region. The shift and broadening near T_N is attributed to the AF magnetization induced in the planes perpendicular to the DM vectors.

dependent and we often refer to H , the approximate ESR magnetic fields instead of the fixed excitation frequency, $\omega_+/2\pi$. We denote the 9.4 GHz ESR data centered at 0.34 T as “low field” and the 111.2, 222.4 and 420 GHz data centered near 4, 8 and 15 T as “high field”. Our low field spectra in the \mathbf{b} direction agree with the low field ESR of Yasin [19] who measured κ -ET₂-Cl in the three principal directions. At low fields the ESR of the A and B layers merge into a single line at the average g factor and linewidth. At high fields there is a single ESR line in the principal directions. For field angle $\varphi_{ab} \approx 45^\circ$ in the (\mathbf{a}, \mathbf{b}) plane the A and B ESR lines are resolved. The field direction is very close to $\mathbf{c} \times \mathbf{D}_A$ and \mathbf{D}_B in the A and B layers, respectively [Fig. 1(c)]. Using the known orientation of the g tensor [20], the lower field ESR line is assigned to the layer with \mathbf{H} roughly parallel to the long ET molecular axis.

Fig. 2 shows the magnetic resonance spectra from the weak ferromagnetic ground state to the high temperature paramagnetic state in 8 T magnetic field parallel to \mathbf{c} . Near T_N , between 22 and 30 K, the resonance broadens beyond observability. The line broadening and shift depend strongly on the direction and magnitude of the magnetic field even in the paramagnetic state above T_N . In Fig. 2 \mathbf{H} is perpendicular to both \mathbf{D}_A and \mathbf{D}_B and the shift and broadening are large.

The field dependence of the ESR line position, H_{res} , shows unambiguously that the interlayer coupling is negligible and the magnetization is induced independently in the A and B layers. The g factor defined by $\hbar\omega_+ = g\mu_B H_{\text{res}}$ is temperature (T) and \mathbf{H} independent above

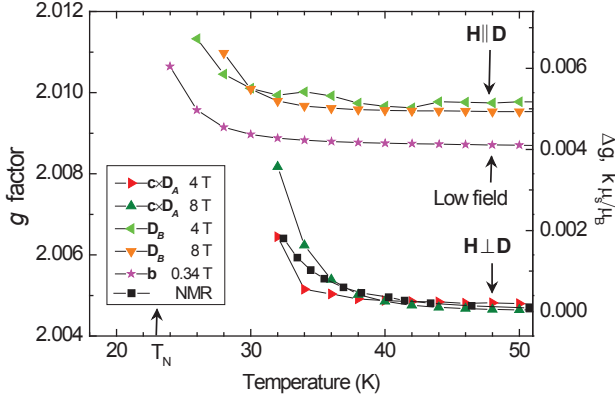


FIG. 3. (Color online) Temperature dependence of the g factors (left scale) and Δg (right scale) in various fields in κ -ET₂-Cl. ■: (right scale) $k\mu_s/\mu_B$ from the ^{13}C Knight shift of Ref. 9 in $H = 7.4$ T along **a** ($H_\perp = 5.2$ T). $k = g_0 DM_0/(8H_\perp)$ relates the ESR shift to the staggered magnetic moment μ_s [see Eq. (3)].

50 K. Fig. 3 displays the T and \mathbf{H} dependence below 50 K. The right scale of Fig. 3 gives the difference $\Delta g = g - g_0$ where g_0 is the g factor at 50 K for $\mathbf{H} \parallel \mathbf{c} \times \mathbf{D}$. In B layers where $\mathbf{H} \parallel \mathbf{D}_B$, Δg is independent of H . In contrast, in A layers where $\mathbf{H} \perp \mathbf{D}_A$, Δg is anomalously field dependent: as $T \rightarrow T_N$ from above, Δg has an upturn at several degrees higher temperatures in high fields than in low field. In usual antiferromagnets the upturn of Δg signifies the onset of magnetic correlations. As discussed later, the field dependence of the g factor is explained by the field induced staggered magnetization. The Δg upturn shifts with field to higher T only in every second layer. The anomalous field dependent g shift arises from magnetic correlations within the A layers. Δg is independent of H in layers with $\mathbf{H} \parallel \mathbf{D}_B$. Even close to T_N , interlayer coupling that would increase the staggered magnetization in B layers is insignificant.

Data on the magnetic-field-induced ESR linewidth are presented in Fig. 4. The half width at half maximum linewidths are determined from a fit to Lorentzian derivative line shapes. The coupling between adjacent layers is very small but not strictly zero. For magnetic fields along $\varphi_{ab} = 45^\circ$, a detailed analysis of the lineshape [21] reveals a small static exchange field proportional to the homogeneous magnetization below 40 K. At 32 K and 7.5 T the interlayer exchange field is antiferromagnetic and about 1 mT. In the present work interplane magnetic coupling was taken into account by fitting the ESR spectra to two Lorentzians with different admixtures of the absorption and dispersion components.

There are two contributions to the linewidth in the paramagnetic state below about 50 K: $\Delta H = \Delta H_0(T) + \Delta H_R(\mathbf{H}, T)$. $\Delta H_0(T)$ is measured at low fields. The anisotropy of $\Delta H_0(T)$ is small [Fig. 4(b)]. $\Delta H_0(T)$

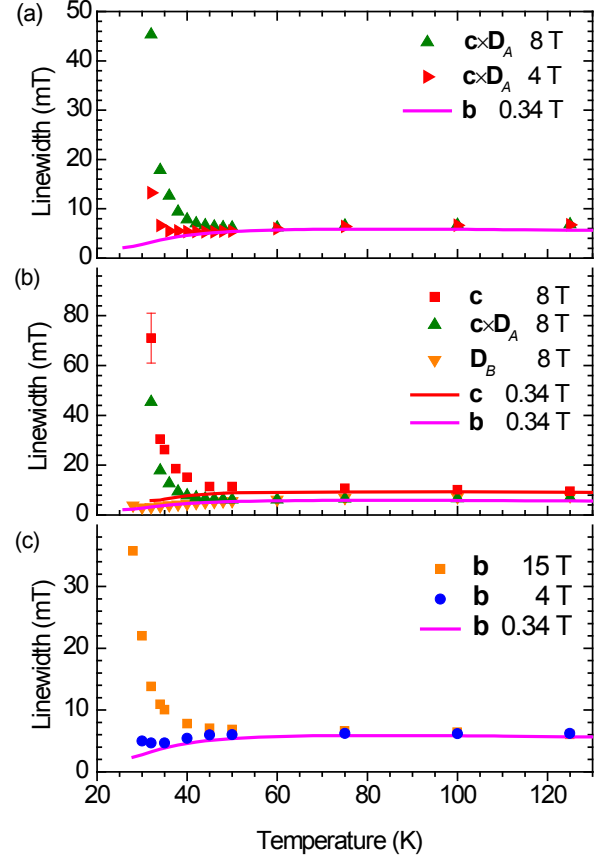


FIG. 4. (Color online) Frequency and magnetic field direction dependence of the ESR linewidth, ΔH . (a) The frequency dependence in the $\mathbf{H} \perp \mathbf{D}$ plane where the field-induced contribution is largest. (b) Dependence on the direction of \mathbf{H} with respect to \mathbf{D}_A . ΔH is frequency independent for $\mathbf{H} \parallel \mathbf{D}$. Data for $\mathbf{H} \parallel \mathbf{c}$ at 0.34 T are from Ref. 19. (c) Frequency dependence of ΔH for $\mathbf{H} \parallel \mathbf{b}$.

increases smoothly with decreasing temperature from 300 K to about 75 K and decreases steeply below 50 K in all directions.

In contrast, the linewidth due to fluctuations of the field-induced staggered magnetization, $\Delta H_R(\mathbf{H}, T)$ rapidly *increases* at high fields as T_N is approached. At fixed temperatures near T_N , the increase of $\Delta H_R(\mathbf{H}, T)$ with \mathbf{H} is stronger than linear [Fig. 4(a)]. $\Delta H_R(\mathbf{H}, T)$ is largest in the plane perpendicular to \mathbf{D} , as shown in Fig. 4(b) for $\mathbf{H} \parallel \mathbf{c}$ and $\mathbf{H} \parallel \mathbf{c} \times \mathbf{D}_A$. On the other hand, there is no field-induced line broadening parallel to \mathbf{D}_B ; ΔH is field independent above 30 K [Fig. 4(b)].

Like the g shift, the field-induced linewidth of individual ET layers is independent of the magnetization in adjacent layers. $\Delta H_R(\mathbf{H}, T)$ is isotropic in the plane perpendicular to the DM vector: it is about the same in the \mathbf{c} direction where $\mathbf{H} \perp \mathbf{D}$ in all layers, and in the $\mathbf{c} \times \mathbf{D}_A$ direction where $\mathbf{H} \perp \mathbf{D}$ in every second layer. In the \mathbf{b} direction the induced linewidth is smaller than the

linewidth induced by fields of the same magnitude along $\mathbf{c} \times \mathbf{D}_A$. It appears from Fig. 4(c) that within experimental precision only the component of \mathbf{H} along $\mathbf{c} \times \mathbf{D}_A$ broadens the line. This also supports that the magnetization is induced independently in adjacent layers since \mathbf{M}_s is the same in all layers for $\mathbf{H} \parallel \mathbf{b}$.

It is natural to assume that $\Delta H_{\text{fl}}(\mathbf{H}, T)$ is dominated by fluctuations of \mathbf{M}_s . Although in general, both longitudinal and transverse fluctuations with respect to the external field increase the linewidth, near T_N \mathbf{M}_s is much larger than the longitudinal magnetization.

We know of no calculations of the ESR linewidth for the 2D anisotropic Heisenberg antiferromagnet. On the other hand, the excitations and the ESR spectrum of the 1D chain were extensively studied [3–6]. The DM interaction in an external magnetic field acts approximately as a staggered magnetic field, $\mathbf{h} = (\mathbf{D}_{12}/J) \times \mathbf{H}$ with an alternating sign for subsequent molecules along the chain [5]. (There is a further small contribution to \mathbf{h} from the in-plane alternating g factor anisotropy). \mathbf{H} induces an anisotropic gap in the excitation spectrum proportional to $(DH)^{1/2}$ for small H . The gap is largest for $\mathbf{H} \perp \mathbf{D}$ and vanishes for $\mathbf{H} \parallel \mathbf{D}$. At low temperatures \mathbf{D} shifts the $q = 0$ ESR mode. Fluctuations of the staggered magnetization at the Larmor frequency at finite wavelengths, q , broaden the ESR. The line broadening is anisotropic and is roughly proportional to h^2/T^2 but absent if $\mathbf{H} \parallel \mathbf{D}$.

The ESR in $\kappa\text{-ET}_2\text{-Cl}$ resembles the ESR in 1D Heisenberg chains with a DM interaction [4], the main difference is that $\kappa\text{-ET}_2\text{-Cl}$ orders at a finite temperature. The similarity with the 1D chain arises from the structure: the DM interaction can be replaced by an effective staggered field, \mathbf{h} that is uniform within lines of dimers along \mathbf{a} but alternates along \mathbf{c} [Fig. 1(b)]. In the mean field approximation the frequencies of the two $q = 0$ modes are [22]:

$$\hbar\omega_- = (hJ\mu_s)^{1/2} \quad (1)$$

$$\hbar\omega_+ = g_0\mu_B H \left(1 + \frac{Jh\mu_s}{2(g_0\mu_B)^2 H^2} \right) \quad (2)$$

to smallest order in h .

The ESR frequency above T_N is given by ω_+ . For $\mathbf{H} \perp \mathbf{D}$ we have $h = HD_{12}/J$ and the magnetic field dependent shift is:

$$\Delta g = g_0(DM_0/8H)\mu_s/\mu_B \quad (3)$$

The measured g shifts are in excellent agreement with Eq. (3). Above T_N , the staggered moment μ_s decreases rapidly with temperature and increases with the component of \mathbf{H} perpendicular to \mathbf{D} . Moreover, μ_s in similar fields, measured from Δg and from the NMR Knight shift [9] agree well (Fig. 3).

We suggest that the magnetic field dependent NMR shift [9] and relaxation rate [16] in $\kappa\text{-ET}_2\text{-Cl}$ are also “2D effects” in the sense that they do not depend on

interlayer coupling. For \mathbf{H} along $\varphi_{ab} = 45^\circ$ the ESR spectra of A and B layers are alternately affected and unaffected by the field and we predict that this is the case for the NMR Knight shift and relaxation also. We propose that the gap in the excitation spectrum, $\hbar\omega_-$ is the reason for the anomalous increase of T^* with field. Close to T_N , until ω_- is larger than the NMR frequency ω_n , fluctuations enhancing the nuclear spin relaxation are suppressed. Above T^* the gap is smaller than ω_n and the fluctuations are restored.

The magnetic-field-induced increase of the static staggered magnetization and magnetic fluctuations in layers with $\mathbf{H} \perp \mathbf{D}$ is undoubtedly a purely 2D effect depending only on intralayer interactions. In layers with $\mathbf{H} \parallel \mathbf{D}$, both the static component of \mathbf{M}_s and its fluctuations are insensitive to the large increase of \mathbf{M}_s in adjacent layers, even at temperatures very close to T_N (Figs. 3 and 4). The absence of correlation between the magnetization of adjacent layers (measured in magnetic fields) suggests that interlayer correlations are unimportant in determining the phase transition temperature T_N (in $H = 0$); and in this sense $\kappa\text{-ET}_2\text{-Cl}$ is a 2D magnet.

Finally we discuss the dimensionality of the phase transition. The absence of correlation between the magnetic order of adjacent layers raises the question whether the phase transition at $T_N = 23\text{ K}$ in the absence of H is driven by the slightly anisotropic intralayer exchange alone, or does the interlayer coupling enforce order in the third direction? Below T_N the weak ferromagnetism of isolated layers have a twofold degeneracy in $H = 0$. The full 3D ordering (i.e., along the third direction) under cooling in $H = 0$ below T_N is an open question. It may be ferromagnetic, antiferromagnetic, and it may happen at any temperature below T_N , but we believe it must be very sensitive to crystalline imperfections. In our experiments under magnetic fields the degeneracy is lifted even in the $\mathbf{H} \parallel \mathbf{D}$ layers by misalignment of the field, the g factor anisotropy between layers and other small anisotropic effects. Thus, as the temperature is lowered there is a crossover to a weak ferromagnetic phase. In the experiment of Ref. 9 the ferromagnetic order was enforced at low temperatures by a magnetic field prior to the determination of T_N in $H = 0$.

We are indebted to F. Mila and K. Penc for stimulating discussions and acknowledge the Hungarian National Research Fund OTKA NN76727, CNK80991, CK84324, K107228, the New Hungary Development Plan TÁMOP-4.2.2/B-10/1–2010-0009, and the Swiss NSF and its NCCR “MaNEP”.

* atj@szfki.hu

[1] D. Mattis, *The Theory of Magnetism Made Simple* (World Scientific, 2006).

- [2] J. Fröhlich and E. H. Lieb, Phys. Rev. Lett. **38**, 440 (1977).
- [3] D. C. Dender, P. R. Hammar, D. H. Reich, C. Broholm, and G. Aeppli, Phys. Rev. Lett. **79**, 1750 (1997).
- [4] S. A. Zvyagin, A. K. Kolezhuk, J. Krzystek, and R. Feynherm, Phys. Rev. Lett. **95**, 017207 (2005).
- [5] M. Oshikawa and I. Affleck, Phys. Rev. Lett. **79**, 2883 (1997).
- [6] I. Affleck and M. Oshikawa, Phys. Rev. B **60**, 1038 (1999).
- [7] K. Kodama, S. Miyahara, M. Takigawa, M. Horvatić, C. Berthier, F. Mila, H. Kageyama, and Y. Ueda, Journal of Physics: Condensed Matter **17**, L61 (2005).
- [8] U. Welp, S. Fleshler, W. K. Kwok, G. W. Crabtree, K. D. Carlson, H. H. Wang, U. Geiser, J. M. Williams, and V. M. Hitsman, Physica B **188**, 1065 (1993).
- [9] F. Kagawa, Y. Kurosaki, K. Miyagawa, and K. Kanoda, Phys. Rev. B **78**, 184402 (2008).
- [10] J. M. Williams *et al.*, Inorganic Chemistry **29**, 3272 (1990).
- [11] A. M. Kini *et al.*, Inorganic Chemistry **29**, 2555 (1990).
- [12] A. Antal, T. Fehér, A. Jánossy, E. Tátrai-Szekeres, and F. Fülöp, Phys. Rev. Lett. **102**, 086404 (2009).
- [13] D. F. Smith, S. M. De Soto, C. P. Slichter, J. A. Schlueter, A. M. Kini, and R. G. Daugherty, Phys. Rev. B **68**, 024512 (2003).
- [14] D. F. Smith, C. P. Slichter, J. A. Schlueter, A. M. Kini, and R. G. Daugherty, Phys. Rev. Lett. **93**, 167002 (2004).
- [15] K. Miyagawa, A. Kawamoto, Y. Nakazawa, and K. Kanoda, Phys. Rev. Lett. **75**, 1174 (1995).
- [16] I. J. Hamad, A. E. Trumper, P. Wzietek, S. Lefebvre, and L. O. Manuel, Journal of Physics: Condensed Matter **17**, 8091 (2005).
- [17] K. Nagy, D. Quintavalle, T. Fehér, and A. Jánossy, Applied Magnetic Resonance **40**, 47 (2011).
- [18] B. Náfrádi, R. Gaál, T. Fehér, and L. Forró, Journal of Magnetic Resonance **192**, 265 (2008).
- [19] S. S. Yasin, *Electron Spin Resonance in Low-Dimensional Spin Chains and Metals*, Ph.D. thesis, 1. Physikalisches Institut der Universität Stuttgart (2008).
- [20] T. Nakamura, T. Nobutoki, T. Takahashi, G. Saito, H. Mori, and T. Mori, J. Phys. Soc. Jpn. **63**, 4110 (1994).
- [21] A. Antal, T. Fehér, E. Tátrai-Szekeres, F. Fülöp, B. Náfrádi, L. Forró, and A. Jánossy, Phys. Rev. B **84**, 075124 (2011).
- [22] J.-B. Fouet, O. Tchernyshyov, and F. Mila, Phys. Rev. B **70**, 174427 (2004).